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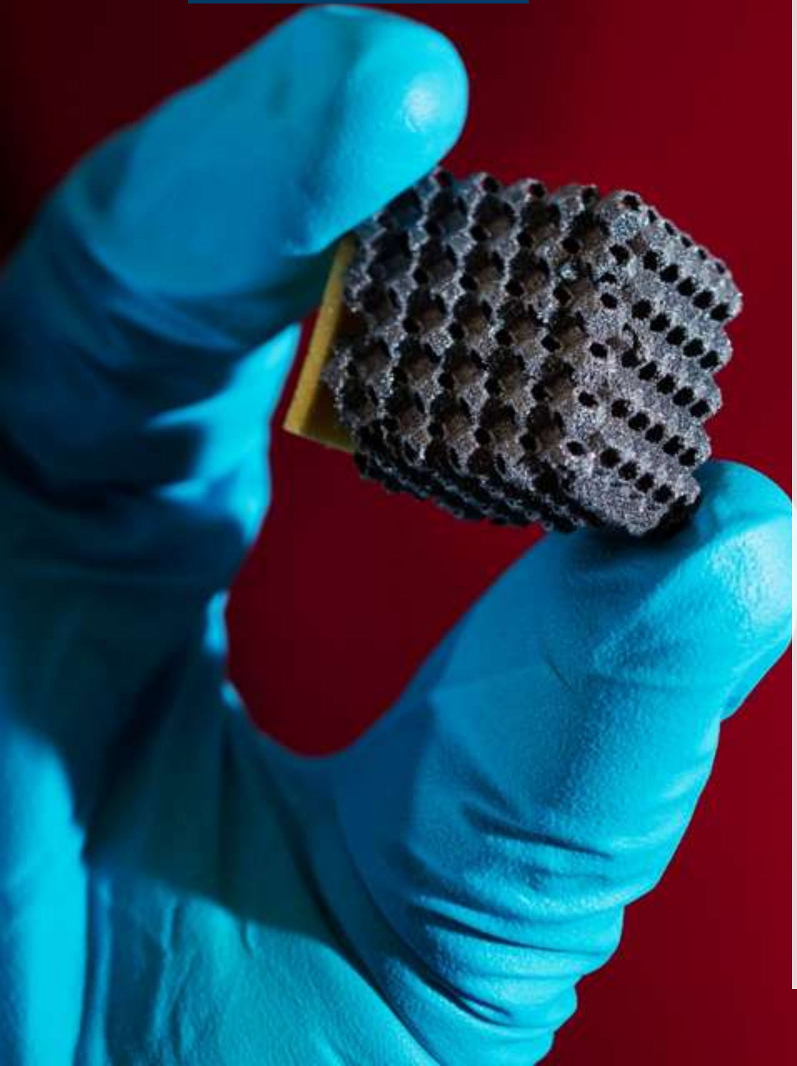

Development of 3D printed amine grafted silica adsorbents for CO_2 capture – adsorbent preparation, performance and potential applications

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Outline:

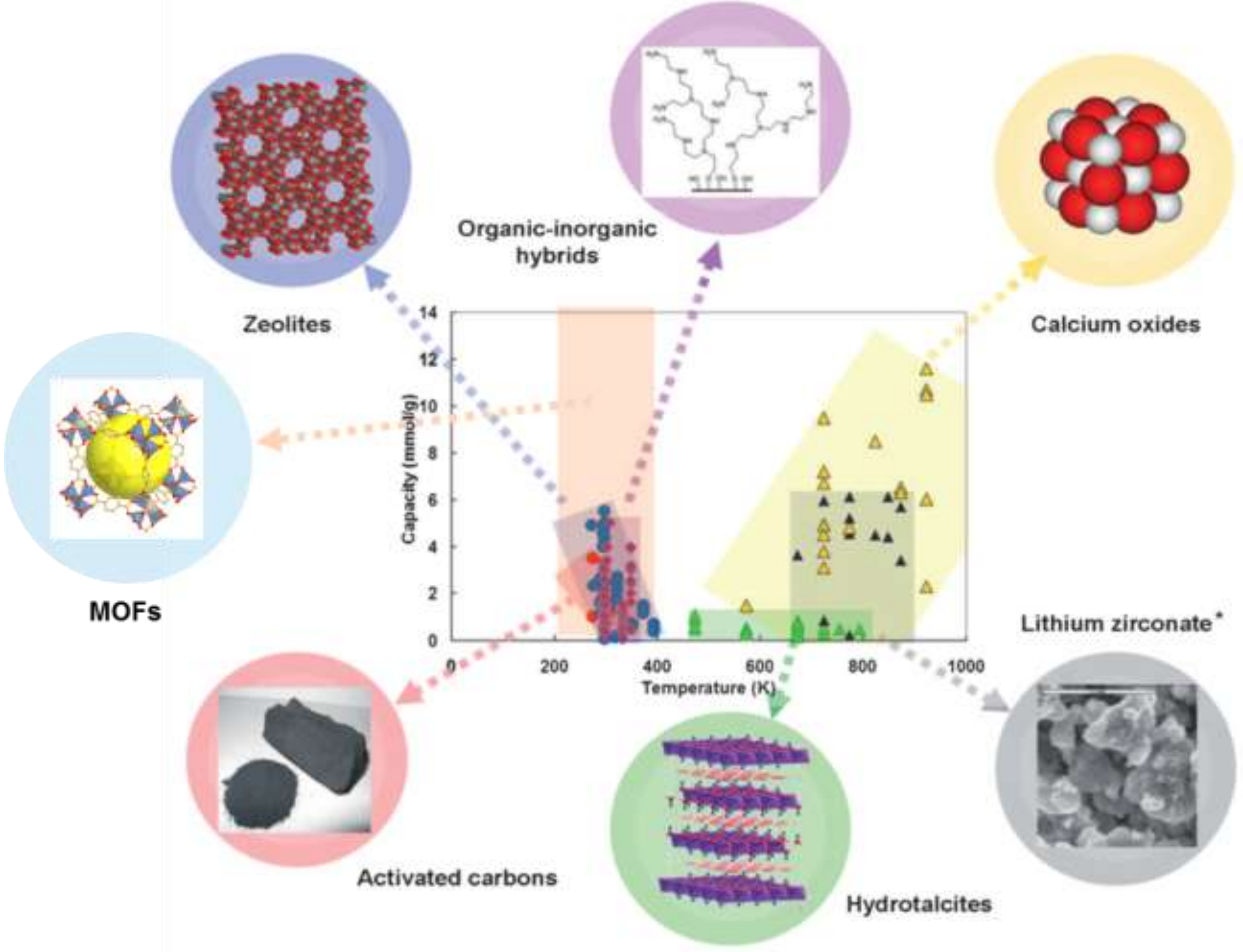
- Why CO_2 capture by solid adsorbents?
- Why 3D-printed adsorbents?
- How do we make the 3D-printed adsorbents and how do they work?
- A post-combustion case comparing a VSA process using traditional pellets vs. 3D-printed adsorbents
- Some final remarks

Why CO_2 capture by solid adsorbents?

- A good solid adsorbent is a high surface area material with high physical and chemical stability under the relevant conditions, that
  - can fast adsorb significant amounts of CO_2 selectively over the other gases present, and,
  - can fast release CO_2 either by lowering the partial pressure of CO_2 or by heating the adsorbent.

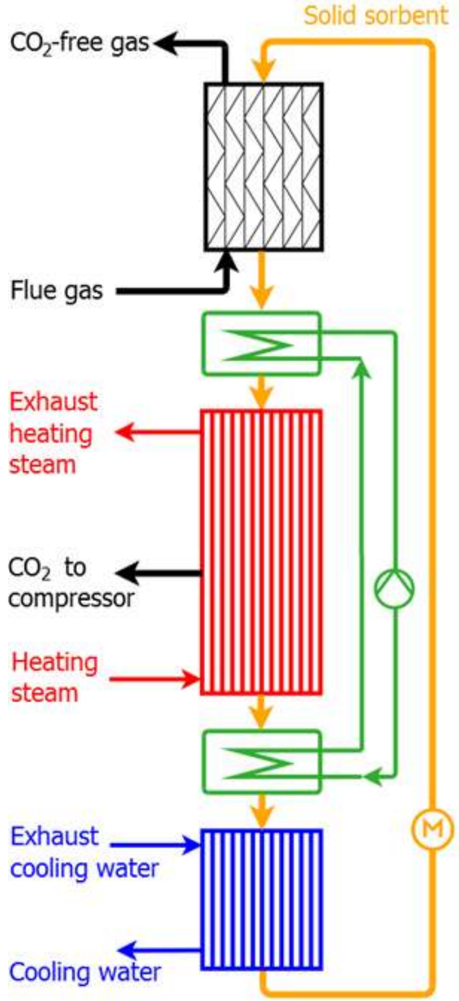
✓ **In principle – low energy requrements for regeneration !**

✓ **Mostly – low environmental impact**

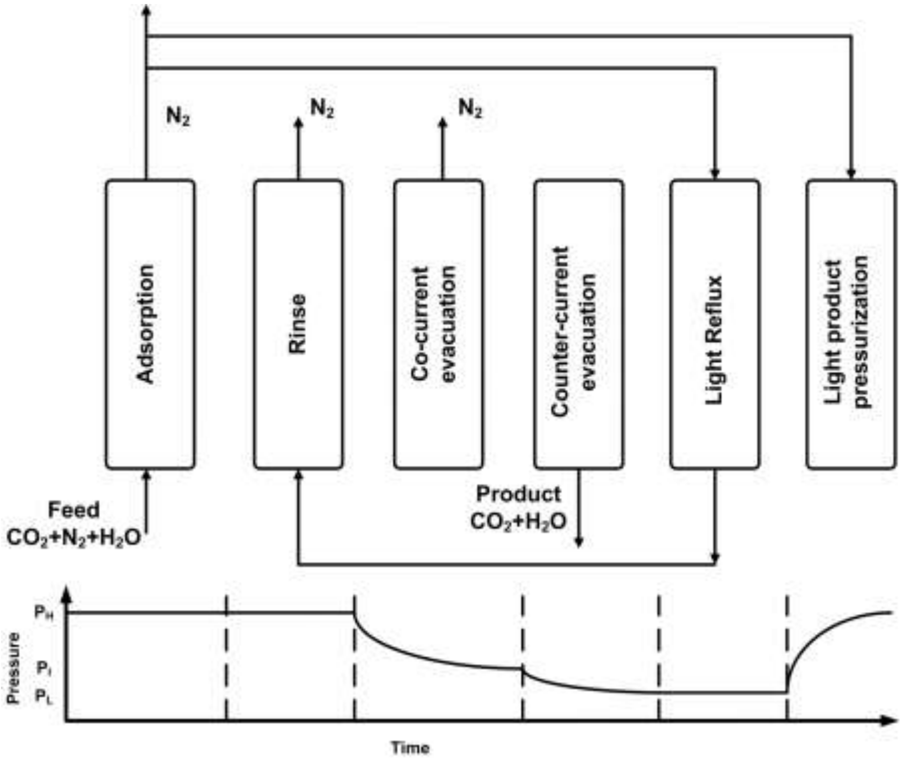


Why CO_2 capture by solid adsorbents? Contd…

- In a process utilizing solid adsorbents, the solid adsorbent material is operating between an adsorpion phase and a desorption (regeneration) phase, either by moving the powder between different zones, or by changing the atmosphere around the solid adsorbent:
  - PVSA - Pressure-vacuum swing adsorption
  - TSA - Temperature –swing adsorption



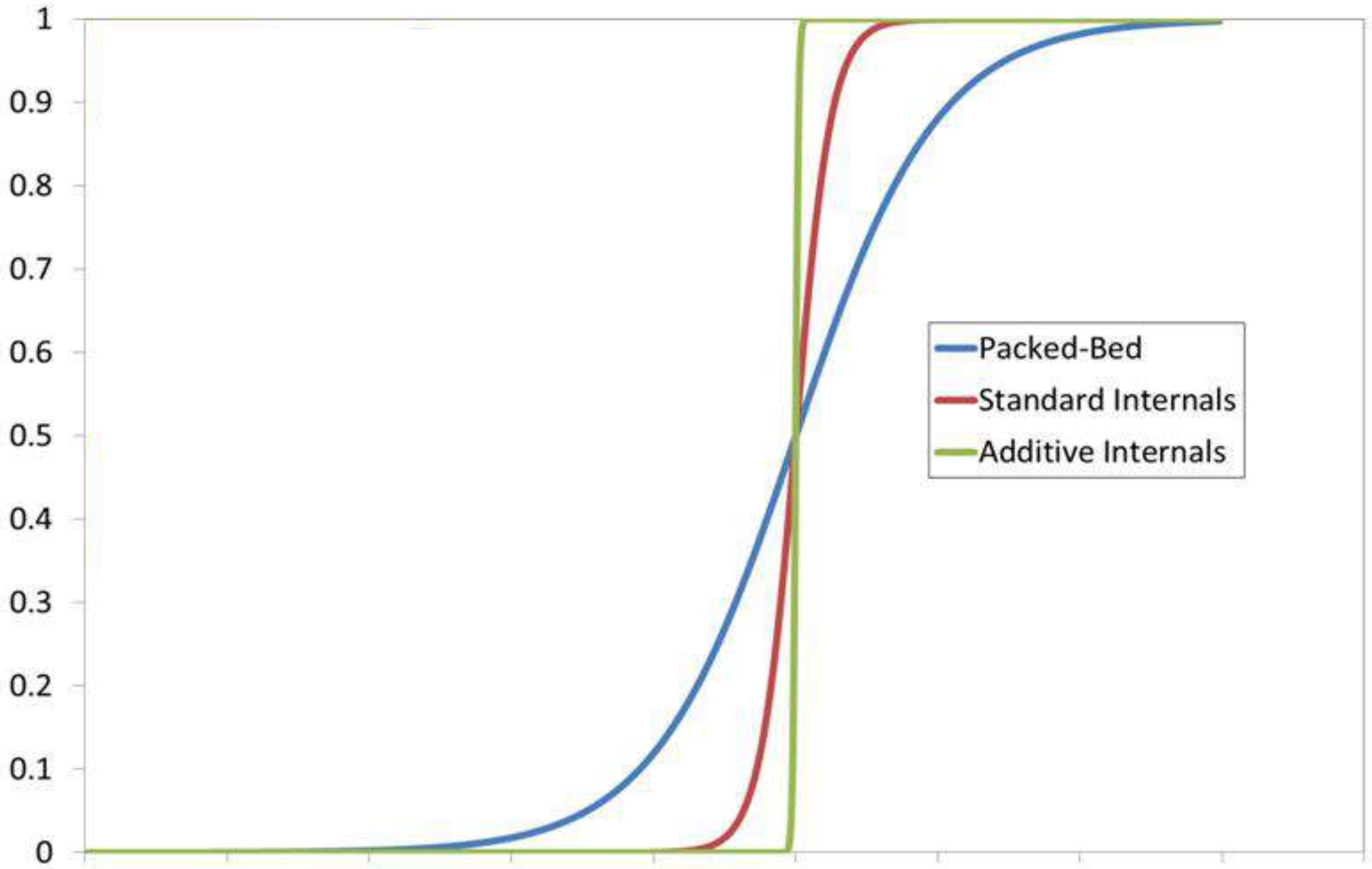
Moving bed concepts
TSA



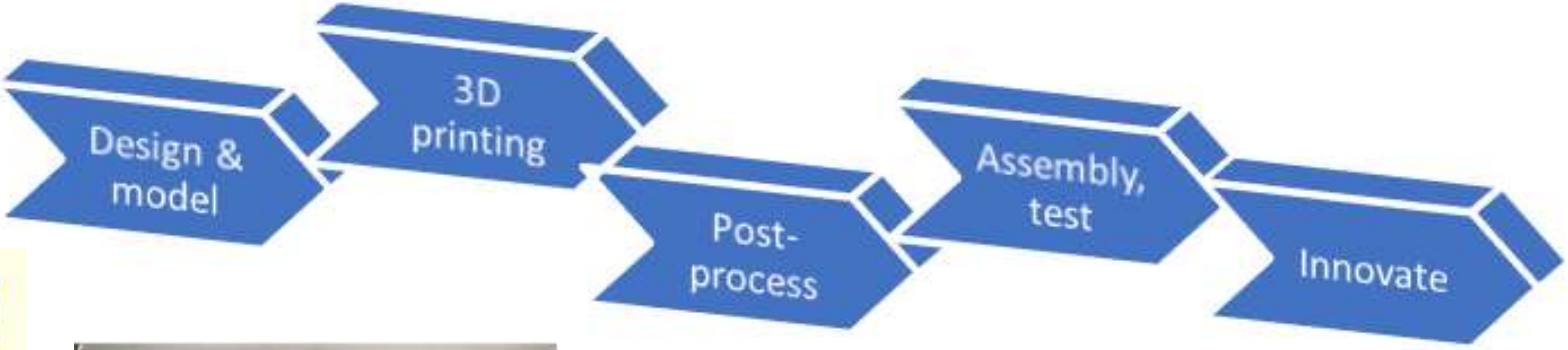
Multiple fixed bed concepts:
PSA, VSA, PVSA, TSA

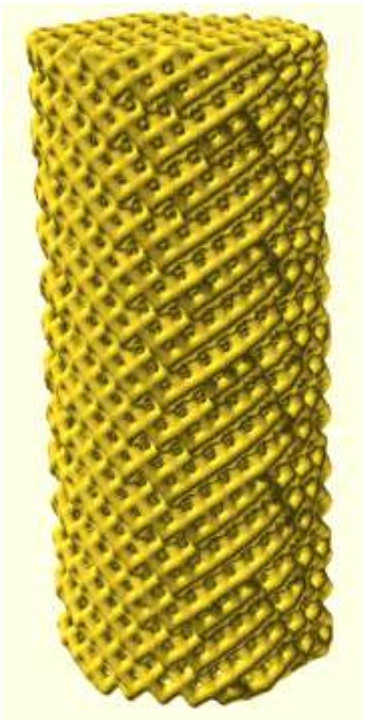
Why 3D-printed adsorbents?

- CO_2 capture processes using solid adsorbents can have low energy requirements, but have often huge footprints!
- One way to lower the process footprint is to:
  - Increase gas flow, and/or
  - shorten the cycle time
- This will require lower pressure drop and sharper mass-transfer through the adsorbent bed.

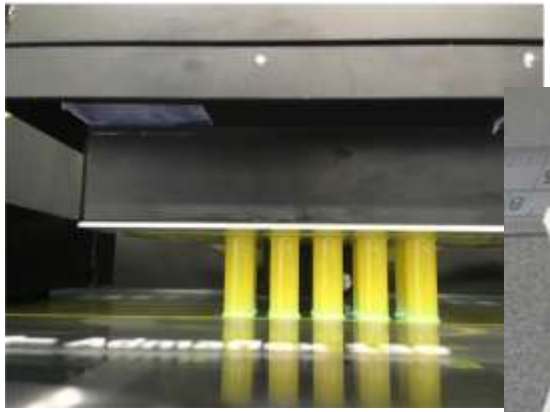


How 3D-printed adsorbents?

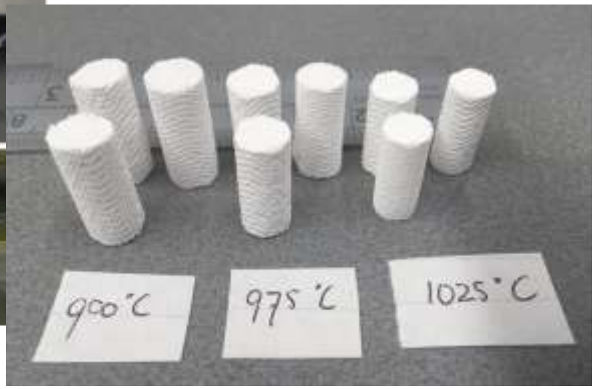




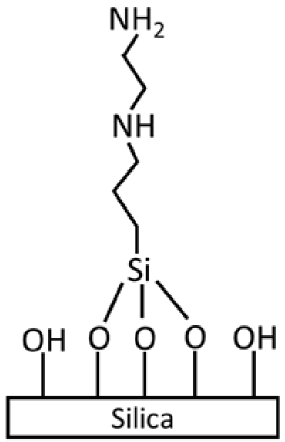
Optimized 3D foam model



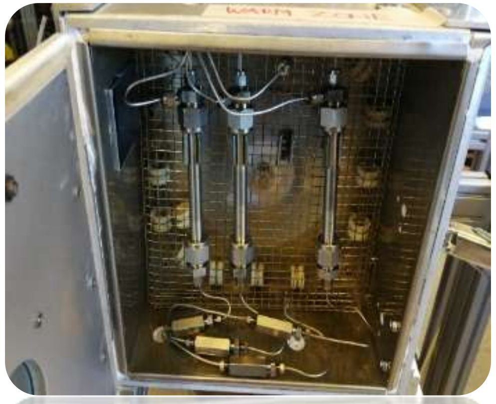
3D printing of foam structure



Thermal post-treatment

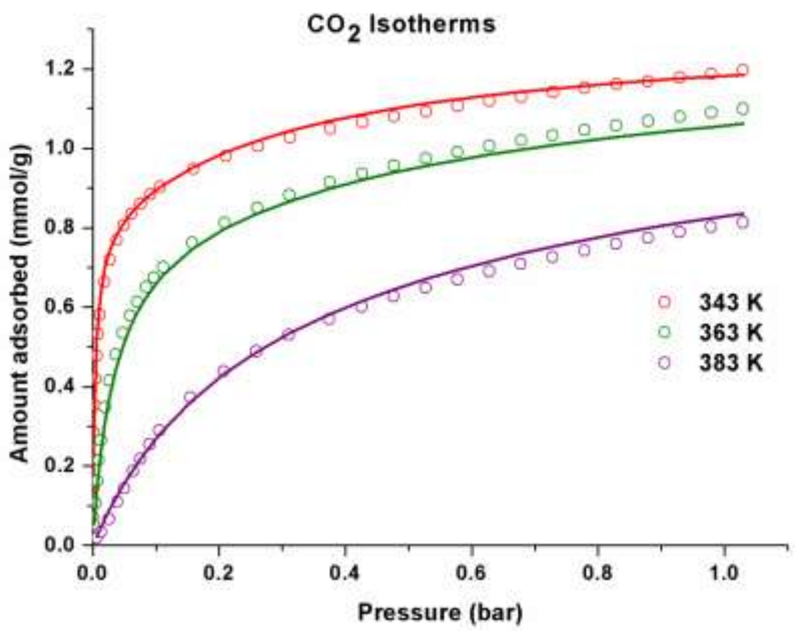


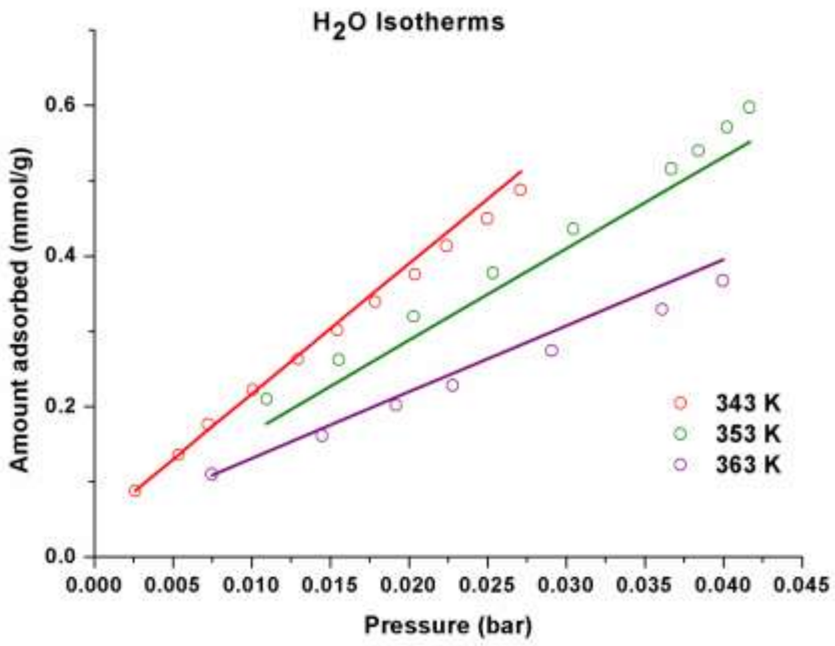
Grafting amine moieties

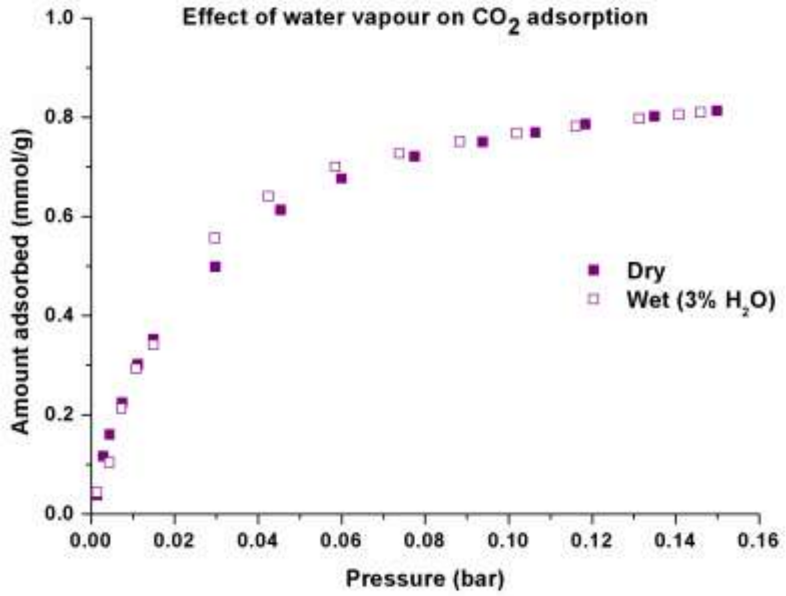


Testing in automated setup

Adsorption equilibria: Single component and ternary isotherms

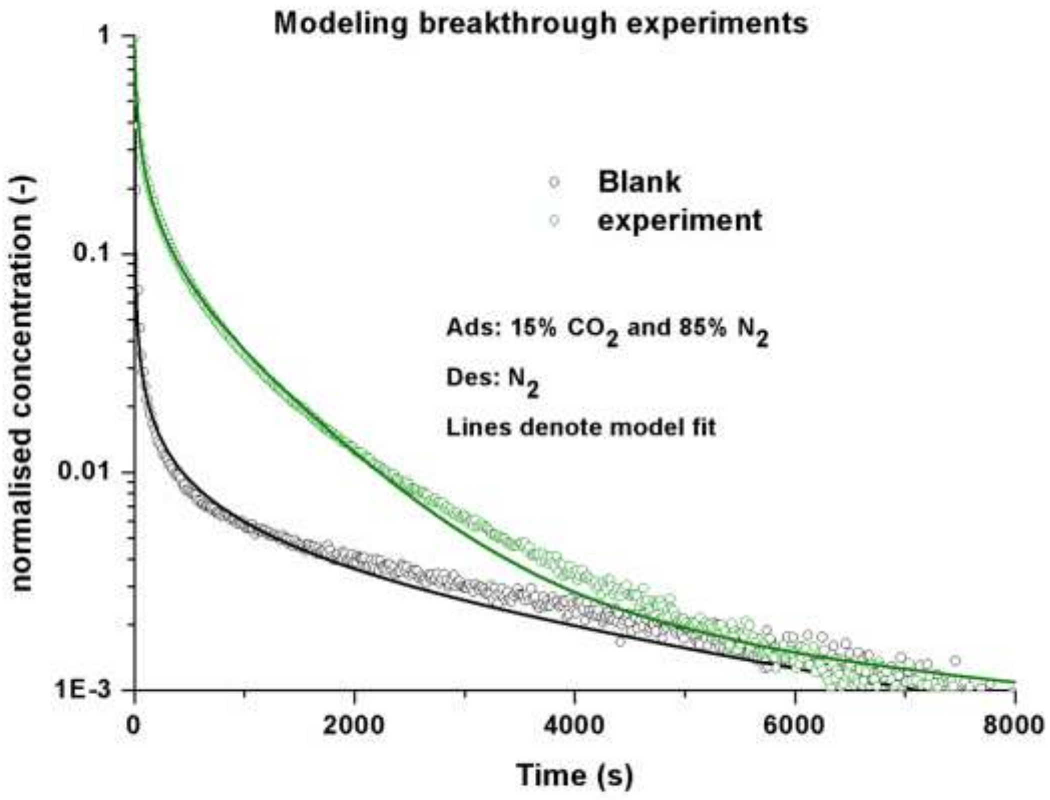


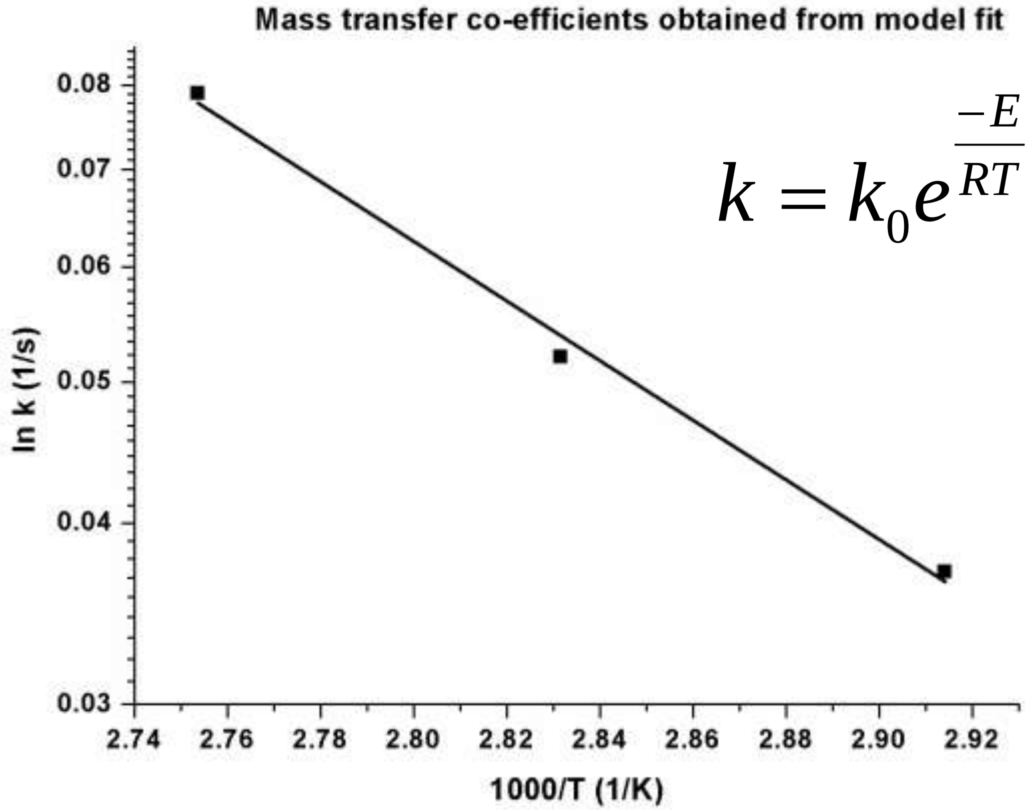




- Single component CO_2 and H_2O isotherms from volumetric apparatus
  - Acceptable CO_2 capacity: 0.7 mol/kg at 0.15 bar and 363 K
  - Heat of adsorption: –111 kJ/mol CO_2 and -39 kJ/mol H_2O
- Ternary CO_2 (15% CO_2 3% H_2O 82% N_2) isotherms from column breakthrough experiments
  - Water does not affect CO_2 adsorption

Adsorption kinetics: Column breakthrough experiments





$$k = k_0 e^{\frac{-E}{RT}}$$

- Column breakthrough (dynamic experiment) at different flow rates
  - Empty column runs to estimate system dead volume
  - Packed column runs followed by empty column tests
- Minimize residual between experiments and model by fitting mass transfer co-efficient

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A real case: post-combustion coal fired power plant

Feed gas: 15% CO_2 5% H_2O 80% N_2, 363 K, 1 bar
Assumptions

- CO_2 adsorption in un-affected by water (same as pure component adsorption)
- H_2O isotherm described by competitive dual-site Langmuir isotherm
- Nitrogen is considered inert
- Mass transfer-coefficients are estimated from breakthrough experiments

Pellet vs 3D printed adsorbent properties
Diameter of pellet = 2 mm

Diameter of the 3D printed adsorbent = 0.1 m
Channel width of the 3D printed structure = 0.3 mm

Pressure drop correlation:
Pellets[1]

$$\frac{-dP}{dZ} = 180\left(\frac{(1-\varepsilon)}{\varepsilon}\right)^2 \frac{v\mu}{d_p^2}$$

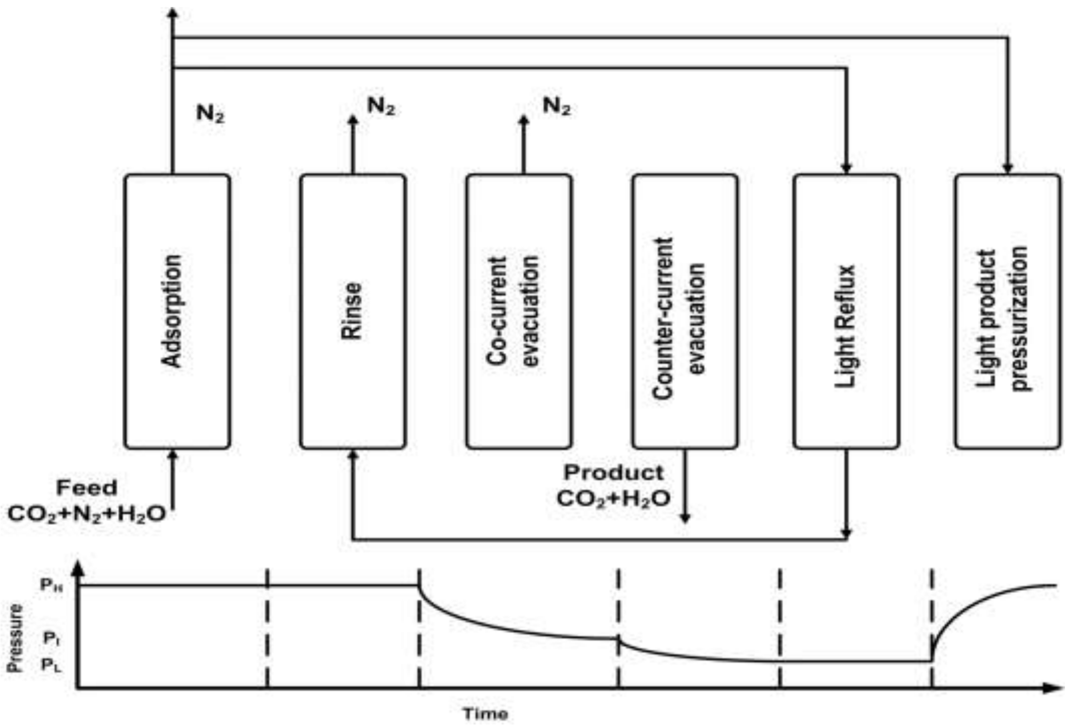
3D printed[2]

$$\frac{-dP}{dZ} = 3.84\frac{v_{channel}\mu}{d_{channel}^2}$$

Pressure drop measured in literature[3] also used to demonstrate improvement in performance

[1] Nikolic and Kikkinides *Adsorption* (**2015**) 21:283–305
[2] Patton et al., *Chem Eng Res Des*, 82(A8): 999–1009
[3] Rebelo et al.,Chemical Engineering & Processing: Process Intensification 127 (2018) 36–42

Process optimization

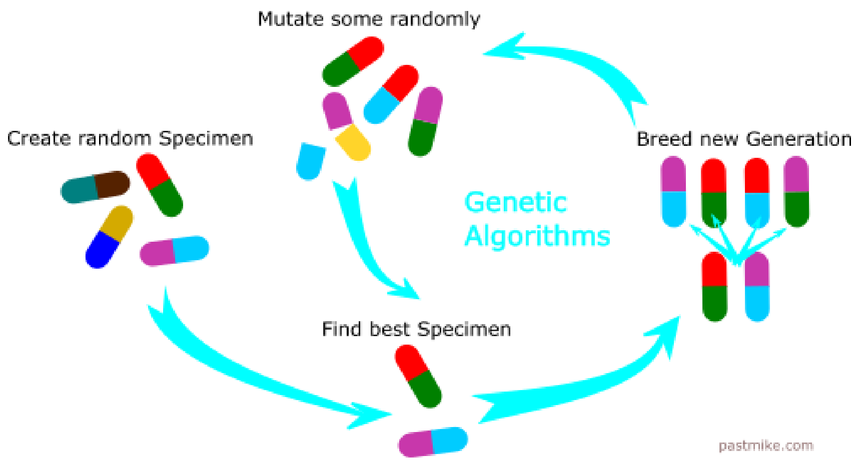


- Process performance defined by
  - CO_2 purity (>95%), CO_2 recovery (>90%), specific energy and productivity
  - Variables affecting performance are: step durations, pressures and feed flow rates
- Aim :
  - To identify optimum operating conditions with minimum specific energy and maximum productivity.
  - To compare the performance of 3D printed adsorbents with reference pellets with same capacity.
- Genetic algorithm based optimization to obtain best performance

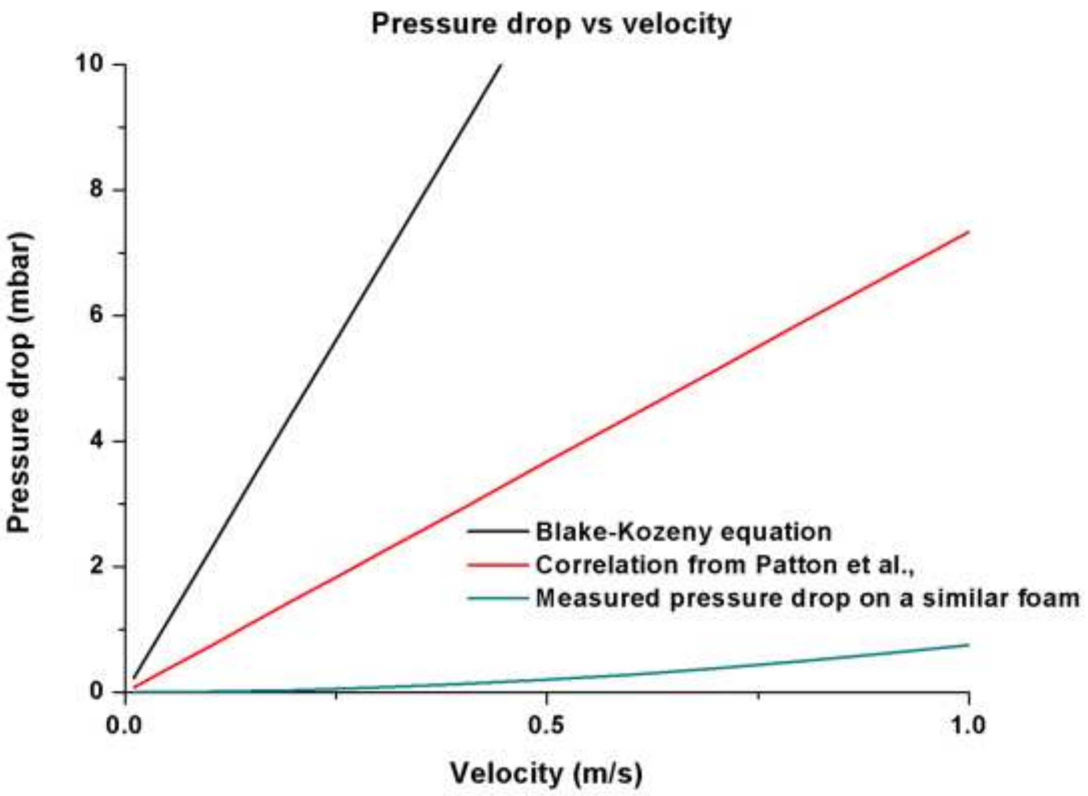
$$CO_2\ \text{purity} = \frac{\text{mass } CO_2 \text{ in evac}}{\text{total mass evac}} \qquad CO_2\ \text{recovery} = \frac{\text{mass } CO_2 \text{ in evac}}{\text{mass } CO_2 \text{ in feed}}$$

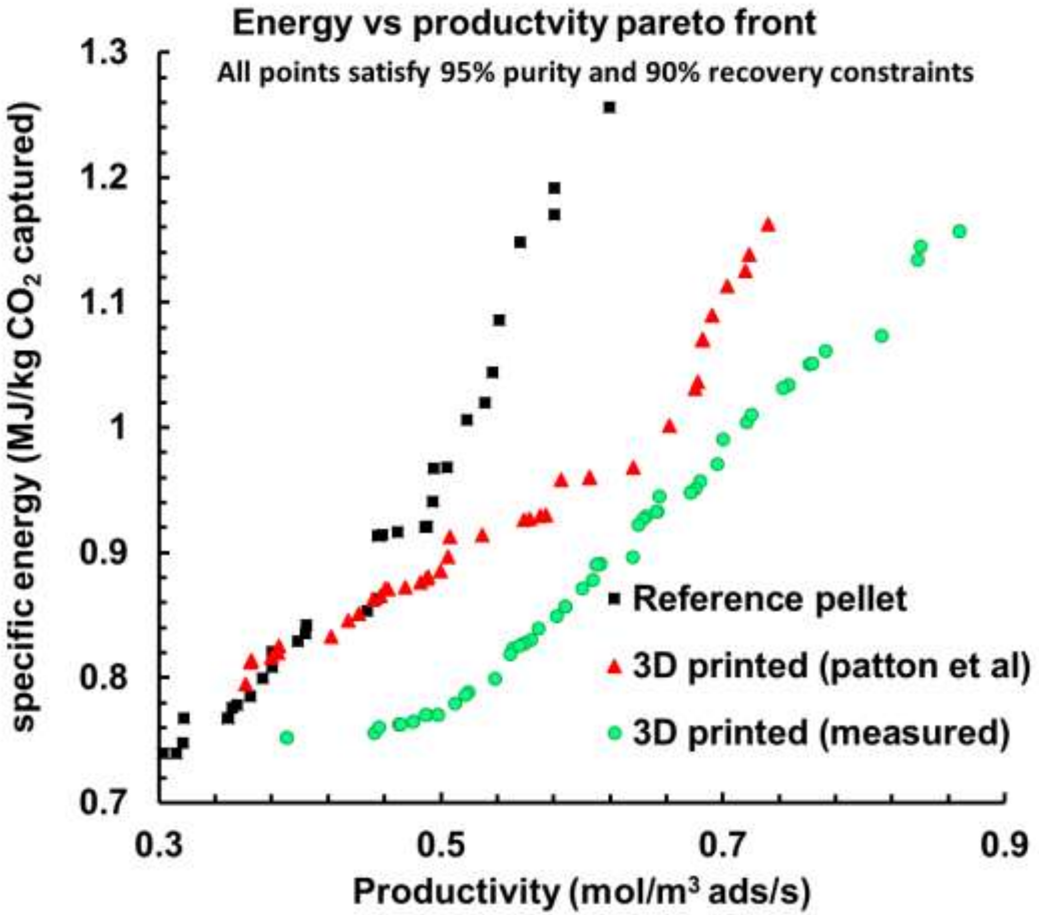
$$\text{Specific energy} = \frac{\text{Compression+Evacuation energy}}{\text{mass } CO_2 \text{ in evacuation}}$$

$$\text{Productivity} = \frac{\text{mass } CO_2 \text{ in evacuation}}{\text{volume of adsorbent X cycle time}}$$



Results of the optimization





- Improvement in productivity observed with 3D printed materials due to lower pressure drop

Final remarks

- Amine grafted silica showed good capacity un der both dry & wet conditions at temperatures around 70-100 °C.
- VSA process optimization show that improvements in both process productivity and energy consumption can be obtained with 3D printed adsorbents compared to standard pelletized sorbents.
- The improved performance is mainly a consequence of lower pressure drop for an optimized 3D-printed structure compared to pellets
- Further work:
  - Improve fabrication procedure for the 3D-printed sorbents!
  - Measure pressure drop across the 3D printed adsorbent and perform rigourous optimization
  - Study the effect of water vapour at higher partial pressures

Acknowledgements

The ACT 3D-CAPS project # 271503 has received funding from RVO (NL), RCN (NO), UEFISCDI (RO), and is co-funded by the CO_2 Capture Project (CCP) and the European Commission under the Horizon 2020 programme ACT, Grant Agreement No 691712

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Thanks
For your kind attention !